Accumulation of cadmium and uranium in arable soils in Switzerland

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Abstract

Mineral phosphorus (P) fertilizers contain contaminants that are potentially hazardous to humans and the environment. Frequent mineral P fertilizer applications can cause heavy metals to accumulate and reach undesirable concentrations in agricultural soils. There is particular concern about Cadmium (Cd) and Uranium (U) accumulation because these metals are toxic and can endanger soil fertility, leach into groundwater, and be taken up by crops. We determined total Cd and U concentrations in more than 400 topsoil and subsoil samples obtained from 216 agricultural sites across Switzerland. We also investigated temporal changes in Cd and U concentrations since 1985 in soil at six selected Swiss national soil monitoring network sites. The mean U concentrations were 16% higher in arable topsoil than in grassland topsoil. The Cd concentrations in arable and grassland soils did not differ, which we attribute to soil management practices and Cd sources other than mineral P fertilizers masking Cd inputs from mineral P fertilizers. The mean Cd and U concentrations were 58% and 9% higher, respectively, in arable topsoil than in arable subsoil, indicating that significant Cd and U inputs to arable soils occurred in the past. Geochemical mass balances confirmed this, indicating an accumulation of 52% for Cd and 6% for U. Only minor temporal changes were found in the Cd concentrations in topsoil from the six soil-monitoring sites, but U concentrations in topsoil from three sites had significantly increased since 1985. Sewage sludge and atmospheric deposition were previously important sources of Cd to agricultural

soils, but today mineral P fertilizers are the dominant sources of Cd and U. Future Cd and U inputs to agricultural soils may be reduced by using optimized management practices, establishing U threshold values for mineral P fertilizers and soils, effectively enforcing threshold values, and developing and using clean recycled P fertilizers.

Keywords

Cadmium, uranium, agricultural soils, mineral fertilizer, phosphorus, soil contamination, regulation

Capsule

Past accumulation of Cd and U and ongoing accumulation of U in agricultural soils, point to the need to use “clean” P fertilizers.

1. Introduction

Phosphate (P)-containing mineral fertilizers contain trace elements that are potentially hazardous to humans and the environment (Kratz et al., 2016; McLaughlin et al., 1996; Schnug and Lottermoser, 2013). Agricultural productivity and ecosystem services can be negatively affected by the use of phosphate-containing fertilizers because of the undesirable amounts of heavy metals added to soil in the fertilizers (Mar and Okazaki, 2012). Metals that are mobile and available to plants may be transferred to crops, groundwater, and surface water (McLaughlin et al., 1996; Schnug and Lottermoser, 2013; Wilcke and Dohler, 1995). Cadmium (Cd) and Uranium (U) may be important impurities in mineral P fertilizers, and there is particular concern about these metals being added to soil in fertilizer because they are toxic (Camelo et al., 1997; Mar and Okazaki, 2012; McLaughlin et al., 1996). Heavy metal concentrations in mineral P fertilizers vary widely depending on the origins of the phosphate rocks used to produce the fertilizers and the nature of the finished fertilizers. For example, Cd concentrations (per kilogram of P) from 1 to >640 mg kg^{-1} have been found in fertilizers (McLaughlin et al., 1996; Ulrich et al., 2014). Phosphate rocks are relatively insoluble in water, so they are processed to make fertilizers. Radionuclides and heavy metals become concentrated during these processes, and can reach 1.5 times the concentrations found in the unprocessed ore (Sattouf, 2007).

The problem of Cd in fertilizers accumulating in soils has been investigated in a number of studies in Sweden (Bengtsson et al., 2003), Germany (Boyson, 1992, Knappe et al., 2008; Wilcke and Döhler, 1995), the Netherlands (Moolenaar and Lexmond, 1998), England and Wales (Nicholson et al., 2003), Australia (Mann et al., 2002), New Zealand (Gray et al., 1999; Schipper et al., 2011) and its general implications for soil, environmental and human health (deVries et al., 2005; Moolenaar et al., 1997; Oborn et al., 2003) and plant uptake (Johnston and Jones, 1992) were assessed. It is well known that Cd in fertilizers can accumulate in agricultural topsoils and that the amount that accumulates depends on the fertilization rate, the crop rotation used, and the properties of the soil (Mann et al., 2002; McLaughlin et al., 1996). Mineral P fertilizer is the main source of Cd to a soil if the fertilizer is applied regularly (Keller

and Schulin, 2003; Moolenaar and Lexmond, 1998). Cd is also added to soil by the application of manure and atmospheric deposition (Nicholson et al., 2003). In the past, the application of sewage sludge may also have added Cd to soil (Kabata-Pendias and Mukherjee, 2007; Keller et al., 2005), but applying sewage sludge to soil is now prohibited in many countries, and was prohibited in Switzerland in 2006. Cd is predominantly removed from soil through the harvesting of crops and, depending on the properties of the soil, the leaching of Cd to deeper soil layers. It has recently been found that current Cd soil budgets in the European Union and Norway are almost in balance (Six and Smolders, 2014). These authors suggested that Cd concentrations in soils will decrease over the next few decades. However, this conclusion was based on average values for Europe, and Cd concentrations in soils will not necessarily decrease in areas with particular crop rotations and fertilization regimes.

Relatively little information is available on the behaviour of U in soils derived from P fertilizers. U may become enriched in topsoils (Takeda et al., 2006; Wetterlind et al., 2012) but can be mobile and leach into groundwater and surface water (Schnug and Lottermoser, 2013; Schnug et al., 2005; Iurian et al., 2015). Mineral P fertilizer is the main source of U to agricultural soils, and manure or sewage sludge application and atmospheric deposition are minor sources (Bottcher et al., 2012; Kabata-Pendias and Mukherjee, 2007; Kratz et al., 2008). Kratz et al. (2008) found that U inputs from manure or sewage sludge are 13%–45% of U inputs in mineral P fertilizers containing the same amounts of P. Plants take up relatively little U from soil, but U in soil can sorb to roots and enter the food chain in root vegetables (ATSDR, 2013; Kratz et al., 2008). However, humans ingest negligible amounts of U in plant products, and it has been suggested that drinking water is the main source of human U uptake (Schnug and Lottermoser, 2013; Schnug et al., 2005). While some studies stated that concentrations of U in drinking water vary regionally and are generally related to the geological bedrock (CCME, 2011; Stalder et al., 2012), other studies found that (depending on soil properties) fertilizer derived U will not significantly accumulate in soils, but is readily transferred to aquifers (Birke and Rauch, 2008; Huhle et al., 2008; Smidt et al., 2012).

A number of factors, listed below together with their trends, need to be considered when assessing the importance of mineral P fertilizers in the accumulation of Cd and U in agricultural soils.

1. As in many European countries the amount of mineral P fertilizer used has decreased significantly since the 1990s in Switzerland (Spiess, 2011). For instance, 16562 t of mineral P fertilizer was applied to agricultural land in Switzerland in 1990, reducing to 4206 t in 2013 (BLW, 2014).
2. Mineral P fertilizers are predominantly applied where crops with high P demands are grown and insufficient animal manure is available to meet the P demands of the crops.
3. Several mineral P fertilizers contain high concentrations of Cd and U (Gisler and Schwab, 2015; Nziguheba and Smolders, 2008). In a recent Swiss survey, 45% of all the mineral P fertilizers analysed contained Cd concentrations higher than the Swiss threshold (50 mg kg^{-1} P), and the highest concentration was 220 mg kg^{-1} (Gisler and Schwab, 2015). No thresholds for U in fertilizers have yet been set. Swiss fertilizers have been found to have relatively high median and maximum U concentrations, of 291 and 485 mg kg^{-1} P_2O_5, respectively (Gisler and Schwab, 2015).

In two recent studies, Fitzgerald and Roth (2015) and Roth and Fitzgerald (2015) concluded that Cd concentrations in the fertilizers used in Switzerland need to be as low as possible because some sections of the population already have Cd intakes close to the tolerable daily intake. They also concluded, because of the toxicity of U, that U concentrations in fertilizers should be more closely monitored than they are currently. Better information on the fates of Cd and U in mineral fertilizers added to soils is needed than is currently available because such information will be required to allow rational debates about managing fertilizer quality in Switzerland and achieving long-term decreases in risks caused by agricultural activities.

In the study described here, we compared Cd and U concentrations in topsoil samples from agricultural and grassland sites and in topsoil samples and subsoil layers (C horizon) at agricultural sites. The aim was to determine whether Cd and U have accumulated in topsoils at arable sites compared to topsoils at grassland sites to which smaller amounts or no mineral

P fertilizers have been added. In a second trial, topsoils of arable sites were compared to or than in deeper soil layers at the same sites, to assess Cd and U accumulation by input from the surface. We also determined Cd and U concentrations in archived soil samples from selected soil monitoring sites in Switzerland that have, in the past, received regular mineral P fertilizer, and calculated Cd and U budgets for the sites over a 25-year period. The aim of the study was to attempt to answer the following questions.

I. Are higher Cd and U concentrations found in arable soils than in grassland soils to which little or no mineral fertilizer has been applied?

II. Are Cd and U more enriched in topsoils than in subsoils?

III. What are the main sources of Cd and U to the arable soils, and are Cd and U still being accumulated appreciably?

IV. What political measures should be taken to decrease Cd and U inputs to soils from mineral P fertilizers?

2. Materials and methods

2.1. Study sites

Cd and U concentrations in about 400 archived soil samples from Switzerland were determined. The samples were from 216 agricultural sites in areas in which mineral P fertilizers are used on arable land. The sites were chosen using georeferenced farm census data that allowed areas containing arable farms to be identified (Figures 1 and S1). Arable farms do not generally have access to sufficient animal manure to provide the nutrients required by arable crops, so we presumed that mineral P fertilizers are predominantly applied on arable farms. Archived soil samples were available from the Swiss soil monitoring network (NABO; from which soil samples collected from 34 arable sites between 2005 and 2009 were available), the Swiss biodiversity monitoring network (BMN; 65 arable sites and 38 grassland sites between 2011 and 2013), the Canton of Aargau (15 arable sites in 2006), the Canton of Solothurn (39 arable sites between 1995 and 2005), and the Canton of Fribourg (25 arable sites between 2007 and 2011). Except for the BMN samples, each archived soil sample was made up of at

158 least 25 individual topsoil (0–20 cm deep) cores from within a 10 m^2 x 10 m^2 square mixed
159 together (Hämmann and Desaules, 2003). Subsoil samples were obtained from soil profiles at
160 the soil monitoring network sites.
161 The BMN archive contained topsoil samples (individual 0–20 cm deep cores from within a
162 circle of radius 5 m at each site) but no subsoil samples. We therefore compared Cd and U
163 concentrations in topsoil samples from arable sites with Cd and U concentrations in topsoil
164 samples obtained from grassland sites (Figure S2), because little or no mineral fertilizer is
165 generally applied to grassland systems in Switzerland. We selected archived soil samples
166 from five soil surveys conducted at the same sites between 1985 and 2009 at six NABO sites
167 to allow temporal changes in Cd and U concentrations in topsoil to be evaluated. The surface
168 soil samples (0-20 cm) were taken every 5 years from the same 10 m^2 x 10 m^2 plot. Each
169 time, two composite samples were generated by mixing 25 individual topsoil cores equally
170 distributed over the plot, to account for the spatial variability of the soils. The mean value for
171 the two composite samples is reported. The mean relative standard deviation between the
172 metal concentrations in the two samples was 6.1% for Cd and 2.6 % for U and was within the
173 analytical error. Thus we assume that our sampling design was suitable to compensate for
174 spatial variations. Annual land management data (including fertilization practices) provided by
175 farmers were available for the NABO sites. The design of the NABO network was described
176 in detail by Gubler et al. (2015).

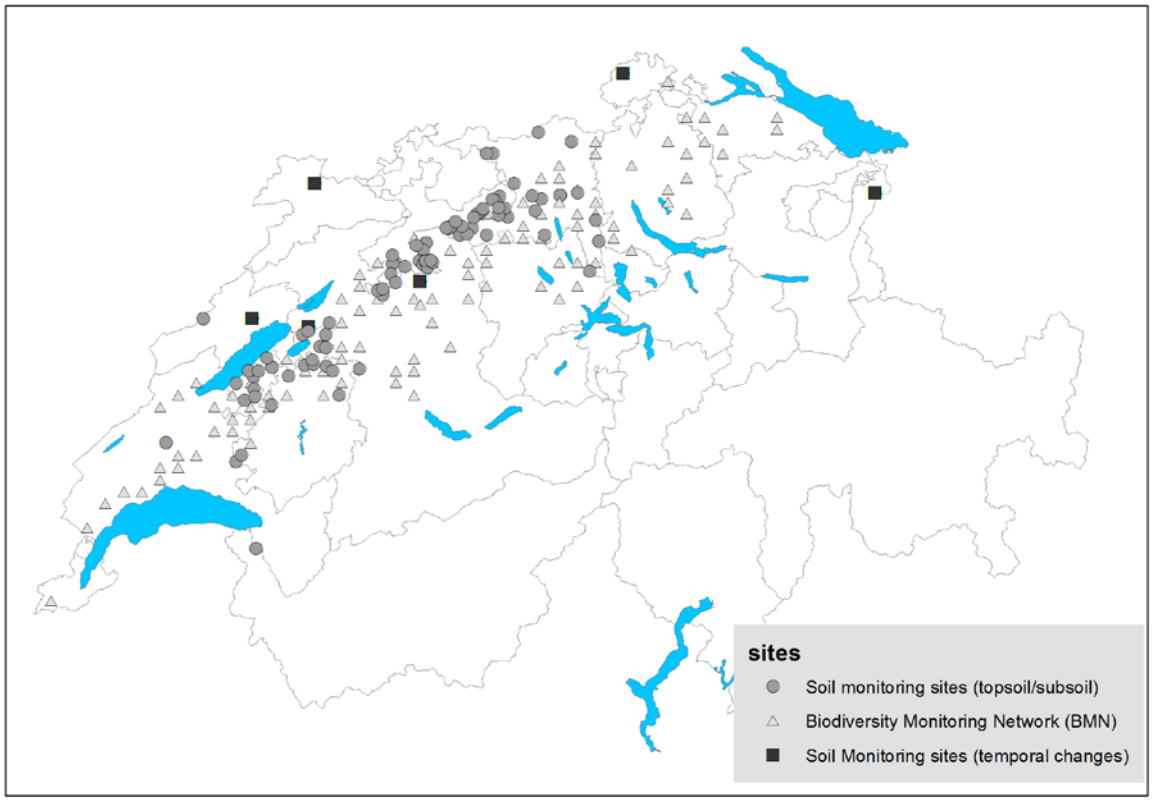


Figure 1. Map of Switzerland showing the locations of the selected sites. The Cd and U concentrations in topsoil and subsoil from the soil monitoring sites (circles) were compared, as were the Cd and U concentrations in topsoil samples from the biodiversity monitoring network arable sites and grassland sites (triangles). Temporal changes in the Cd and U concentrations in soil samples collected from six soil monitoring sites (squares) between 1985 and 2009 were evaluated. The study sites were on the Swiss plateau because little arable farming occurs in the Jura mountains to the north or in the Alps to the south (see Figure S1).

2.2. Analysis

Each soil sample was air dried and passed through a 2 mm sieve. A representative subsample was then ground in an agate mortar. A 0.2 g aliquot was then digested in a mixture of 2 ml 69% HNO_3, 2 ml 48% HF, and 1.5 ml 30% H_2O_2 in a microwave oven at 200 °C, then 10 ml 6% H_3BO_3 was added and the sample was heated to 180°C to complex the residual HF. The Cd and U concentrations in the digest were determined using an inductively coupled plasma mass spectrometer (ICP-MS 7700X; Agilent Technologies, Frankfurt am Main, Germany) using Rh and In as internal standards. The Ti concentration was analysed to allow a τ value to be calculated. The τ value is the result of geochemical mass balancing calculations, which

accounts for natural weathering induced enrichment/depletion of an element (Brimhall et al., 1992; more details in the supplementary material). The Cd and U detection limits were 7 and 2 µg kg^{-1}, respectively. The accuracy of the method was assessed by analysing the "San Joaquin soil" reference material (NIST 2709a) 16 times, and the Cd, U, and Ti recoveries were 101%, 96%, and 93%, respectively. The reproducibility of the method was assessed by digesting and analysing 11 soil samples between two and 16 times. The mean reproducibility (as relative standard deviations) for Cd and U was 9.1% and 4.1%, respectively.

2.3. Statistics and budget calculations

Geochemical mass balances (τ values) were calculated following the method described by Brimhall et al. (1992). Annual Cd budgets were calculated for the NABO sites for the period 1985–2013 following the method described by Keller and Desaules (2004) and Keller et al. (2005). The soil surface balances for the six selected NABO sites took into account Cd inputs from animal manure, mineral fertilizers, atmospheric deposition, sewage sludge, and compost and other outputs in harvested crops. The available land management data were described in more detail by Della Peruta et al. (2014). We only calculated inputs of U from mineral fertilizers because other sources of U, such as atmospheric deposition and animal manure, are negligible (Sheppard and Sanipelli 2012). The leaching of U into subsoil and groundwater cannot currently be estimated because reliable adsorption isotherms and measured leaching data are unavailable. Estimating the leaching of U into groundwater will require an adsorption isotherm similar to that derived by Elzinga et al. (1999) for Cd, to allow the mobility of U in the soil to be estimated from the soil characteristics. The output of U from harvested crops was ignored because very little U has been found to be removed in crops; in previous studies <0.1 and <0.35 g ha^{-1} y^{-1} were found to be removed from rapeseed and sugarbeet, respectively (ATSDR, 2013; Kratz et al., 2008). To test for differences between groups a t test for independent (grass-vs. arable land) or dependent (top- vs subsoil) samples as well as a Mann-Whitney U test (for Cd, no variance homogeneity) was performed. Significance levels were highlighted with * (significant, 95%), ** (highly significant, 99%) and *** (very highly significant,

99.9%). The τ values calculation, statistical analyses, and element budgeting are all described in greater detail in the supplementary material.

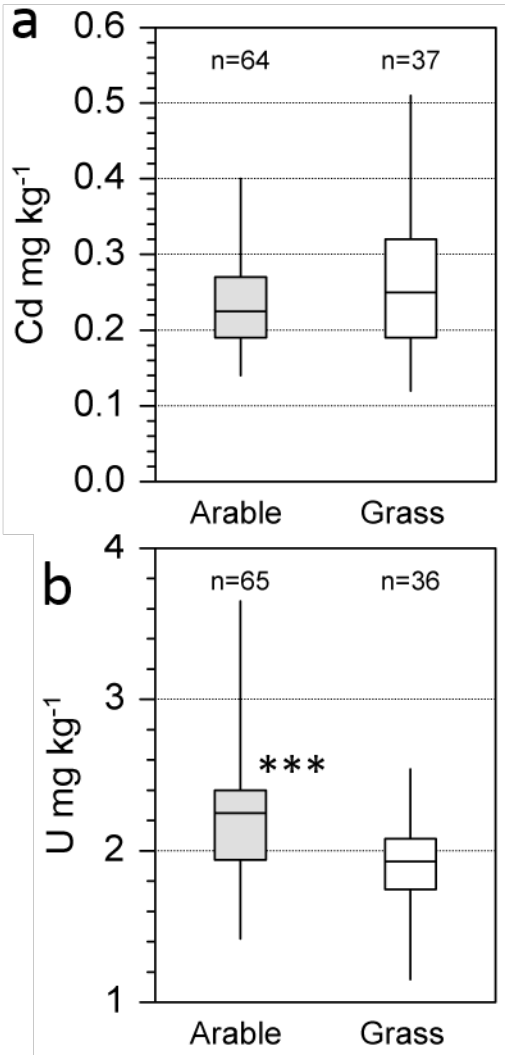


Figure 2. Boxplots of the (a) Cd and (b) U concentrations in soil samples obtained from the Swiss biodiversity monitoring network arable and grassland sites

3. Results

While there was no significant difference between the Cd concentrations in the soil samples obtained from the BMN arable and grassland sites, the U concentrations in the soil samples were very significantly different (Figure 2). The median U concentration in the arable samples was 2.25 mg kg^{-1}, which was 0.32 mg kg^{-1} (16%) higher than the median concentration in the

grassland samples (1.93 mg kg^{-1}). We conclude that U concentrations are higher in arable topsoils to which mineral P fertilizers have regularly been added than in grassland topsoils.

The Cd and U concentrations in the topsoils and subsoils were very highly significantly different (Figure 3). The mean and median Cd concentrations were 0.11 and 0.10 mg kg^{-1} (58% and 62%) higher, respectively, and the mean and median U concentrations were 0.19 and 0.16 mg kg^{-1} (9% and 7%) higher, respectively, in the topsoils than in the subsoils.

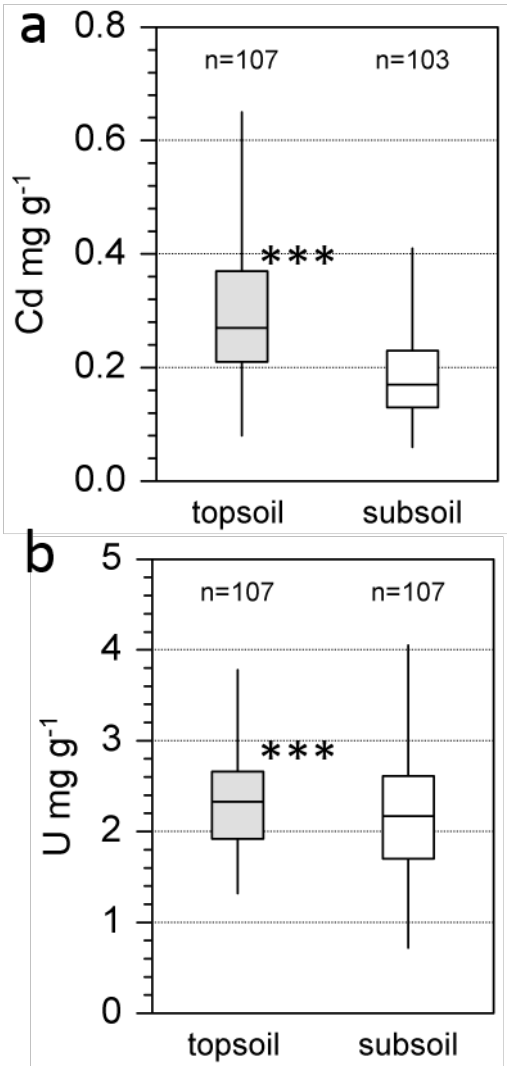


Figure 3. Boxplots of the (a) Cd and (b) U concentrations in the topsoil and subsoil samples

The correlation between the Cd concentrations in the topsoil and subsoil was highly significantly, but the correlation coefficient was relatively small and the slope was only 0.31, indicating that there were Cd inputs from sources other than the parent material. The same was true for U, but the correlation coefficient and slope were both higher (Figure S3). The

correlation between the Cd and U concentrations in the topsoil and subsoil samples suggested that there were two main sources of Cd and U in the soils (Figure 4), namely mineral fertilizers increasing the Cd and U concentrations, and additional sources of Cd (e.g., sewage sludge and atmospheric deposition) increasing the Cd concentrations. The Cd and U τ values were very significantly different from zero (Figure 5), and indicated that Cd accumulation added 52% (mean) or 35% (median) and U accumulation added 6% (mean and median) to the concentrations found in the topsoil. Slightly higher enrichment values were found when the Cd and U concentrations in the topsoil and subsoil samples were compared directly than when the τ values were used, because natural enrichment during weathering was not taken into account in the direct comparison.

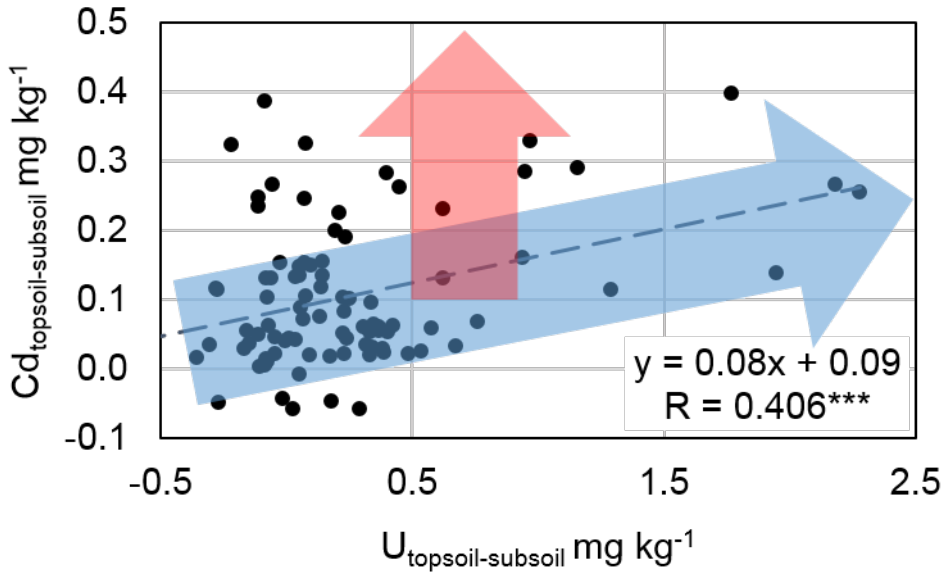


Figure 4. Relationships between the differences between the Cd concentrations in the topsoil and subsoil samples ($Cd_{topsoil}-Cd_{subsoil}$) and the differences between the U concentrations in the topsoil and subsoil samples ($U_{topsoil}-U_{subsoil}$). The blue arrow indicates areas in which Cd and U could have been added to the soil in fertilizer. The red arrow indicates possible contributions from other sources that add more Cd than U to the soil.

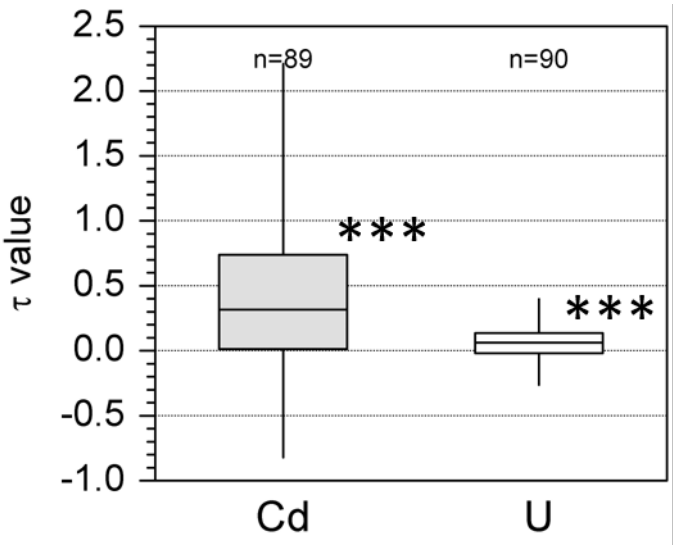
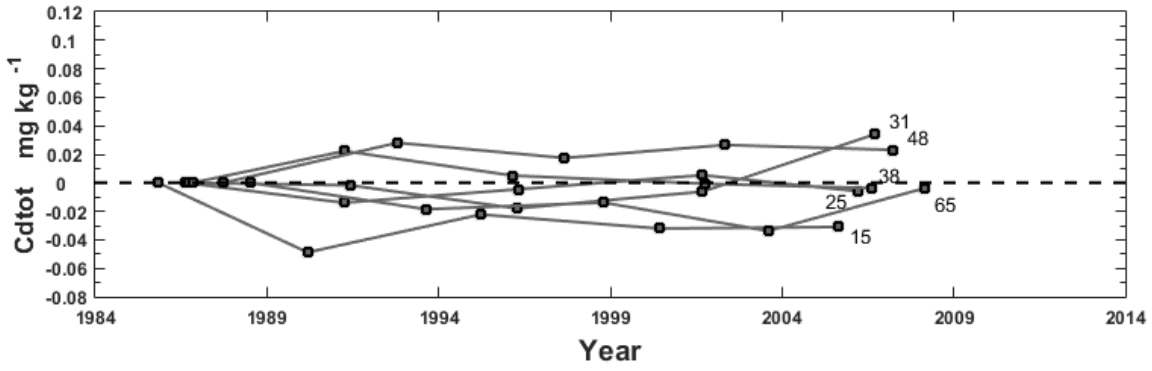


Figure 5. Boxplots of the Cd and U τ values. A τ value of 0 indicates no change in the concentration of the element during weathering, whereas a τ value of 0.5 indicates 50% enrichment and a value of −0.5 indicates 50% depletion (see the supplementary material for further details). The Cd and U τ values were very significantly positive, indicating that both had accumulated in the topsoil samples.

The Cd balances for the six soil monitoring sites showed that Cd inputs in the period 1985–2009 were between 2 and 20 g ha^{-1} y^{-1} (Figures S4–S9). The main source of Cd in the soil was found to be mineral fertilizer. At one site, where triple P mineral fertilizer had regularly been added, Cd inputs were 20–30 g ha^{-1} y^{-1}. Larger amounts of mineral fertilizers were generally applied in the 1980s and 1990s than more recently. The net Cd balance was generally positive, indicating a slight accumulation of Cd (around 0.02 mg kg^{-1} between 1985 and 2009) in the topsoils (Figure 6b). Overall, the surface balance indicated a slight accumulation of Cd at three sites and that the Cd concentration remained stable at each of the other three sites. Repeated soil measurements confirmed the estimated Cd budgets (Figure 6a). Overall, the Cd concentrations in the soil samples increased or decreased only a little between 1985 and 2009.

Inputs of U through mineral P fertilizers at the six monitoring sites were mostly between 10 and 50 g ha^{-1} y^{-1} (Figures S4–S8), but were 100–120 g ha^{-1} y^{-1} at one site where triple P mineral fertilizer was regularly applied. Using the bulk densities of the soil samples and assuming that the added U remained in the topsoil, we calculated that the U concentration increased by 0.1–0.7 mg kg^{-1} between 1985 and 2009 (Figure 6d), a result generally confirmed by the repeated soil measurements (Figure 6c). The U concentrations at four of the six monitoring sites increased by 0.1–0.7 mg kg^{-1}, remained constant at one site, and decreased at another.

a)



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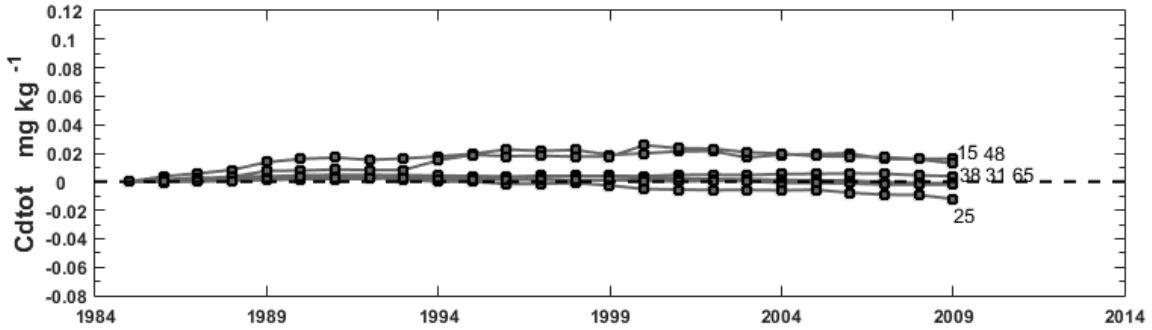

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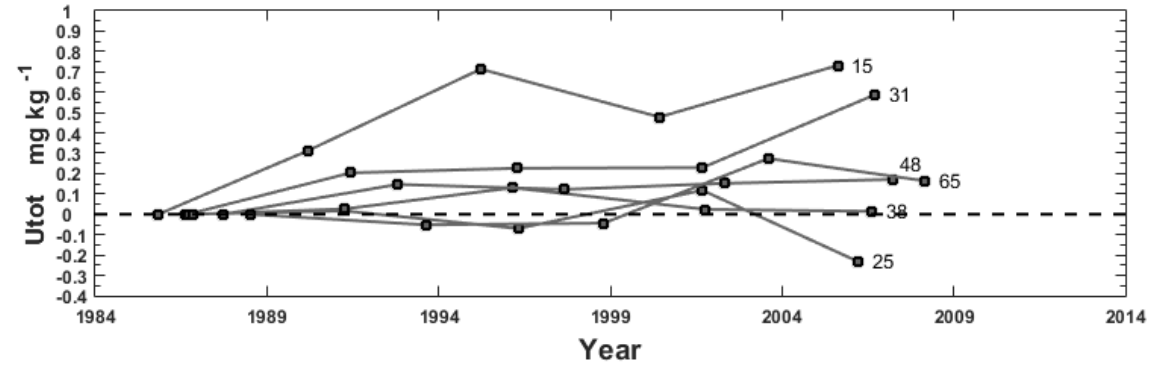

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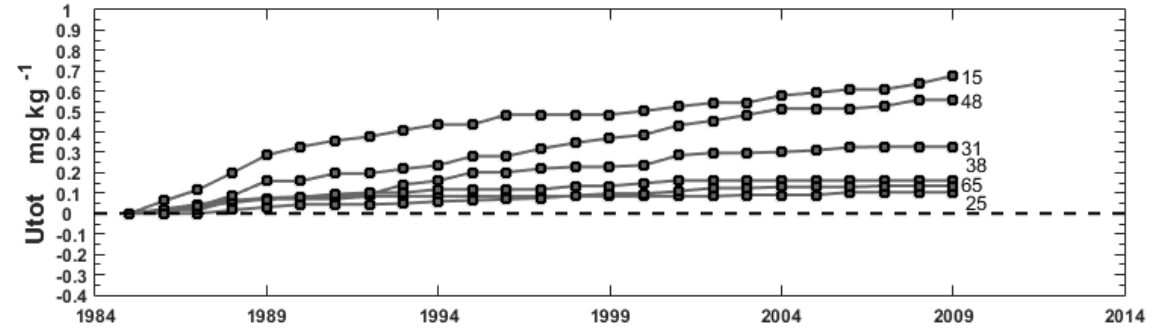

Figure 6. Temporal changes in the Cd and U concentration in topsoil (0–20 cm deep) from the six soil monitoring sites. (a) Cd concentrations in soil samples collected every five years, (b) estimated Cd inputs based on farmers' land management records, (c) U concentrations in soil samples collected every five years, and (d) estimated U inputs in mineral fertilizers based on farmers' land management records.

4. Discussion

4.1. Comparison of Cd and U enrichment in arable and grassland soils

The Cd concentrations in the 65 arable soil samples and 38 grassland soil samples were not significantly different, but U was significantly enriched in the arable topsoils relative to the grassland topsoils (Figure 2). There were a number of possible reasons why Cd was not enriched at the arable sites relative to the grassland sites. Ploughing dilutes Cd in the top soils of arable sites, while high levels of Cd inputs from the atmosphere at times when industrial emissions of Cd were important could have accumulated more effectively in grassland than in arable land. Manure and sewage sludge are more likely to be applied to grassland than arable land, and also smaller amounts of mineral fertilizers are likely to be applied to grassland than arable land, levelling the differences between grass- and arable land. Finally, Cd is taken up by plants, so it is mainly removed from agricultural soils when crops are harvested. This factor affects arable land more than grassland, with a more closed nutrient cycle (McLaughlin et al., 1996; Quezada-Hinojosa et al., 2015).

Negligible atmospheric deposition and plant uptake (and therefore loss through harvested crops) of U occur (ATSDR, 013; Kratz et al., 2008), so, due to the lack of any other credible source we assume that the higher U concentrations in arable topsoils than in grassland topsoils were caused by the long-term application of mineral P fertilizers containing U (Eriksson, 2001; Kratz et al., 2008). It should be noted that some mineral P fertilizer is generally applied to grassland in Switzerland, but much less is applied to grassland than to arable land (Flisch et al., 2009). The U concentrations may be affected by soil properties as grassland soils tend to have higher organic matter contents and lower pH values than arable soils and might sorb U stronger compared to arable soils (Rogasik et al., 2008). The effects of soil management systems, such as tillage, are also important. Ploughing arable land generally mixes the topsoil and subsoil, so enriched U in topsoil will be diluted to some degree depending on ploughing depth. However, this additional factors are probably only of minor importance compared to mineral fertilizer input.

The degree to which we found that U was enriched was similar to the enrichment seen in long-term fertilizer experiments at the Rothamsted Research station in the UK (Rothbaum et al., 1979). The Rothamsted Research experiments have been running since 1843, and in 1976 U was found to be enriched in fertilized plots by a mean of 0.43 mg kg^{-1} relative to control plots. Similar levels of U enrichment have been found in other long-term field experiments, although the actual enrichment levels were somewhat lower because the fertilizer application periods were shorter (Rogasik et al., 2008; Schipper et al., 2011; Taylor and Kim, 2008).

Taylor and Kim (2009) reported Cd and U to be enriched by a factor of 6.45 and 2.53 in arable compared to background (forest) sites. Differences in selection of background sites (grasslands vs. forests) as well as lower atmospheric deposition (Arimoto et al., 1990), but higher Cd and U fertilizer concentrations in New Zeeland (Nauru deposits, McLaughlin et al., 1996) might be the main reason much higher enrichments at the arable sites.

4.2. Enrichment of Cd and U in agricultural topsoils

The Cd and U concentrations in the paired topsoil and subsoil samples clearly indicate the enrichment of Cd and U in the arable topsoils. The enrichment of Cd in arable topsoils relative to subsoils can mainly be attributed to the application of mineral P fertilizer, atmospheric deposition, and in some cases, the historical application of sewage sludge. The atmosphere currently causes only small amounts of Cd to soil, but before effective filters were used to decrease industrial emissions, it provided much more (Heinrichs and Mayer, 1977; Kabata-Pendias and Mukherjee, 2007; Nicholson et al., 1994). Significant amounts of Cd may have been added to the soil at some sites in sewage sludge before the practice was banned in Switzerland in 2006 (Eriksson, 2001; Kabata-Pendias and Mukherjee, 2007; Keller et al., 2005). The Cd concentrations were 58% (mean) higher in the topsoils than in the subsoils, and almost the same result (60% higher concentrations in topsoils than in subsoils) was found in Sweden (Eriksson et al., 1997). The Cd and U concentrations in New Zealand farmed soils in 0-100 mm depth were reported to be enriched by a factor of 1.74 and 1.17 compared to 100-200 mm depth, respectively (Taylor and Kim, 2009), which is a bit higher compared to our

findings. Our results also agreed well with the results of a study in Germany (Uterman and Fuchs, 2008), in which 392 arable, 206 grassland, and 367 forest soils were analysed. In that study, U was relatively more enriched in topsoils than in subsoils at arable sites compared to grassland and forest sites (the median differences between the topsoils and subsoils from arable, grassland, and forest sites were 0.11, 0.09, and −0.04 mg kg^{-1}, respectively). Several researchers have stated that U is predominantly added to agricultural soils in mineral P fertilizers (Bottcher et al., 2012; Kratz et al., 2008; Schnug and Lottermoser, 2013). Considerable amounts of U can be leached from soil, and this can decrease the difference between the U concentrations in topsoil and subsoil (Schnug and Lottermoser, 2013). The τ values confirmed that U was enriched in the topsoil relative to the subsoil (Figure 5). Cd and U are considered to be relatively mobile, so weathering might be expected to deplete these elements in soil. However, we found both to be significantly enriched in the topsoils relative to the subsoils. Given that mineral P fertilizer is the dominant source of Cd and U to soil, and assuming that Cd and U behave similarly during weathering, the degrees to which Cd and U are enriched in topsoil relative to subsoil should correlate. Indeed, we found a highly significant correlation ($r=0.406$; $p < 0.001$) between the differences between the topsoil and subsoil concentrations of Cd and U (Figure 4). However, two general patterns were found. The results for some sites appeared to follow the relationship described above (indicated by the blue arrow in Figure 4), indicating that the Cd and U that had accumulated in these topsoils had the same source. However, for a second group of sites, the differences between the Cd concentrations in the topsoils and subsoils were higher than the differences between the U concentrations in the topsoils and subsoils (indicated by the red arrow in Figure 4). The different degrees to which Cd and U accumulated at these sites could have been caused by differences in Cd inputs from the atmosphere and sewage sludge, different Cd and U concentrations in the fertilizers used, and differences in the dominant routes through which Cd and U were exported from the soils, Cd being predominantly removed in harvested crops and U through leaching (Kabata-Pendias and Mukherjee, 2007; Kratz et al., 2008; Schnug and Lottermoser, 2013).

382 The U concentrations in topsoils on arable land compared to topsoils on grassland were 16%
383 higher, but the topsoils of the arable land were only 6-9% higher than the subsoils. This
384 difference could indicate that U was lost from the topsoils through leaching to deeper soil
385 layers. This process would lower the difference between top- and subsoil, by decreasing topsoil
386 and increasing subsoil concentration. In the opposite in the comparison between topsoils of
387 arable land and grassland, leaching of U would happen at both sites to a similar degree and
388 thus the differences in U concentrations would be higher.
389 About 30% of the τ values are negative, indicating a net loss of U from the topsoil, even though
390 applying fertilizer added U to soil, being an additional indicator for U leaching. A negative τ
391 value could therefore result when U loss during soil development and U leaching are higher
392 than anthropogenic U inputs like P fertilizers.
393

394 ## 4.3. Budgets and trends

395 Cd inputs at all six sites were highest in the late 1980s, then decreased in the 1990s. Only
396 small increases in Cd concentrations were found at four of the six sites (Figure 6). In general,
397 smaller amounts of mineral fertilizers have been applied in Switzerland since the 1990s than
398 were applied before this (Spiess, 2011) because of new fertilizer regulations and agricultural
399 policies aimed at protecting the environment (Herzog et al., 2008). However, apart from this
400 overall trend, fertilization regimes at different sites depend mainly on the crop rotation used
401 and the nutrient requirements of the crops. The Cd and U inputs in mineral fertilizers at the six
402 sites varied greatly over the years (Figures S4–S9) but tended to decrease. This agrees with
403 the results of a study performed by Six and Smolders (2014), who assumed that current
404 environmental and fertilization practices would not lead to any net accumulation of Cd in
405 agricultural soil in the European Union. The temporal changes we found for the six monitoring
406 sites confirmed that little Cd is accumulating in soils in Switzerland. The predicted and
407 measured Cd and U concentrations in the soils generally agreed well except for Cd at site 15.
408 This discrepancy was attributed to the soil at site 15 having been ploughed deeply several

409 times during the study period. Deep ploughing dilutes the Cd in the topsoil and here caused
410 the Cd concentration to decrease over time despite relatively large amounts of Cd being added.
411 The application of mineral fertilizers caused U to accumulate to a considerable degree in soil
412 at three of the six sites (Figure 6c). However, no other sources of U were considered and U
413 export in harvested crops was assumed to be negligible. The U budget was limited by a lack
414 of information on the leaching of U from soil and the sorption of U by soil. There are strong
415 indications that U leaching might be relevant and that the amount of leaching that occurs
416 depends on soil parameters such as the organic matter and clay content and pH (Rogasik et
417 al., 2008). The studied soils show a wide variation in organic matter and clay content as well
418 as in the pH (Table S1), which however did not seem to affect U concentrations in the soil,
419 probably because of the very different amounts of mineral P fertilizers, which overprints
420 differences in U sorption (Figure S4-9). The estimated budgets could therefore only be used
421 to indicate general trends, and soil tillage and leaching were not taken into account. No dilution
422 effect caused by deep ploughing at site 15 was found in the U budget, meaning either that U
423 inputs overcompensated for dilution or that the topsoil and subsoil contained similar U
424 concentrations (because of the natural distribution or leaching of U).
425
426 ## 4.4. Measures to decrease Cd and U inputs in fertilizers
427 Mineral P fertilizers need to be applied efficiently according to the needs of plants, crop
428 rotation, and soil nutrient status, to prevent Cd and U accumulating in agricultural soils. In
429 Switzerland, most of the P requirements of plants are provided by animal manure. Imported
430 mineral fertilizers provided only 15% of the 65,500 t of $P_2 0_5$ applied to crops in 2013. The
431 efficiency at which P is used increased from 22% in the 1980s to 60% in 2013 (BLW, 2013).
432 While all Cd concentrations found in the topsoil samples were still well below the critical loads
433 (mean 2.6 mg Cd kg^{-1} soil) calculated from soil pH and organic matter contents (de Vries et al.
434 2005), there is increasing evidence that Cd concentrations in arable soils and plants have to
435 be kept as low as possible to minimize negative effects on human health (Clemens et al.,
436 2013). For U no critical load approaches are available by now.

Ekardt and Stubenrauch (2013) stated that controlling the use of fertilizers and applying sanctions to traders who do not comply with the law are major challenges to preventing the use of fertilizers containing high concentrations of heavy metals. Laws need to be enforced more strictly to prevent fertilizers that do not comply with the current Cd limits to be applied to the soils (Gisler and Schwab, 2015). Threshold U concentrations for fertilizers may allow U inputs at agricultural sites to be controlled and decreased more effectively than is currently possible. Steps to recover Cd and U could be included in fertilizer production processes (Ulrich et al., 2014). Switzerland is a small country with no sources of mineral P, so it depends entirely on fertilizers produced elsewhere, where any limits for heavy metal concentrations in fertilizers may not be sufficient for Swiss purposes. However, there is some impetus for change, and proposed European Union fertilizer regulations (EC, 2016) will contain strict Cd concentration limits for mineral P fertilizers. Mineral P fertilizers may be substituted with new, more environmentally friendly products prepared from secondary P sources that contain lower heavy metal concentrations than phosphate rock. Such fertilizers may be viable mid- to long-term ways of decreasing Cd and U inputs to soils (Cordell et al., 2009; Hukari et al., 2016; Shepherd et al., 2016). The European Union aims to increase the use of recycled P fertilizers (EC, 2016), and Switzerland has passed a law requiring P to be recovered from P-rich waste, such as wastewater, within the next 10 years (VVEA, 2016). However, depending on the sources and the fertilizer production processes used, such fertilizers may still contain large amounts of potentially toxic trace elements (Kratz et al., 2016; Kumpiene et al., 2016). Further research into the production of sustainable recycled P fertilizers containing low concentrations of pollutants is required.

5. Conclusions

1. Significantly (16%) higher U concentrations were found in arable soils than grassland soils from Switzerland, and we attribute this mainly to the historical application of mineral P fertilizers to arable soils. The Cd concentrations in arable and grassland soils were not

significantly different, probably because of a variety of sources of Cd and the different soil properties and management practices used at these sites.

2. The Cd and U concentrations were higher in topsoil than subsoil, consistent with surface application of Cd and U. While atmospheric deposition and sewage sludge and fertilizer application could have been the sources of Cd, mineral P fertilizer application would have been the main source of U.
3. Mineral fertilizers were likely the dominant sources of additional Cd and U above background levels in fertilized soils. The Cd and U concentrations in these soils remained constant or increased (mostly depending on the amounts of mineral fertilizer applied) between 1985 and 2009.
4. Further decreases in Cd and U inputs to agricultural soils should be enforced by optimizing fertilization practices, better enforcing existing Cd limits, developing new thresholds for U, and increasing the use of clean recycled P fertilizers.

We determined Cd and U concentrations and trends in Swiss arable topsoils for the first time. The results indicate that Cd and U are still accumulating in soils to which mineral P fertilizers are regularly applied. Sources of Cd inputs to agricultural soils and the long-term behaviour of Cd in soils have been investigated in a number of studies, but there is clearly a need for further research into the sources and long-term behaviour of U, particularly into the leaching of U from agricultural soils to groundwater and surface water.

Supplementary material for this article is available online.

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